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EXHIBIT B

ELECTRONIC ENERGY LEVELS FOR ONE-DIMENSIONAL LIQUID 1551

apparent to the investigator as he gains facility using the diagrams.

Denoting configurational average by a subscripted angular bracket, we have

$$\langle (E^*) \rangle_c = N^{-1} \sum_i \langle H_{ii}^2 \rangle_c + 2 \langle H_{ii} H_{i,i+1}^2 \rangle_c + 2 \langle H_{ii} H_{i,i-1}^2 \rangle_c + \langle H_{i+1,i+1} H_{i,i+1}^2 \rangle_c + \langle H_{i-1,i-1} H_{i,i-1}^2 \rangle_c \quad (5A)$$

We may eliminate the summation and the factor N^{-1} since terms whose indices can be made identical by replacing i by $i+j$ are equal to each other. Strictly speaking, this means that we are neglecting end effects

and are considering an infinite chain of square wells. With this assumption, we may write

$$\langle (E^*) \rangle_c = \langle H_{ii}^2 \rangle_c + 2 \langle H_{ii} H_{i,i+1}^2 \rangle_c + 2 \langle H_{ii} H_{i,i-1}^2 \rangle_c + \langle H_{i+1,i+1} H_{i,i+1}^2 \rangle_c + \langle H_{i-1,i-1} H_{i,i-1}^2 \rangle_c \quad (6A)$$

By the same argument we could combine, for instance, terms two and five, although this simplification is not used in Eq. (27). However, terms two and three are not identical, nor is

$$\langle H_{ii} H_{i,i+1}^2 \rangle_c = \langle (H_{ii}) \rangle_c \langle (H_{i,i+1}^2) \rangle_c$$

These latter points can be proved by direct computation using the probability distribution functions (25).

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Solubility of Carbon in Silicon and Germanium

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The solubility of carbon in silicon has been measured over the temperature range 1560 to 2900°C. The enthalpy of solution is 59 ± 3 kcal/mole. A phase diagram for the system Si-C is presented, embodying these solubility data as well as the results of other high-temperature experiments with silicon carbide. It is found that SiC possesses a peritectic point at $2830 \pm 40^\circ\text{C}$. These studies were carried out in argon at pressures as high as 35 atmos. Solubilities of carbon in germanium were measured in the temperature range 2780 to 3170°C, at argon pressures up to 55 atmos, and a tentative phase diagram is given.

EXPERIMENTS WITH SILICON

Introduction

NEITHER the solubility of carbon in silicon at high temperatures, nor the phase diagram of the system Si-C is known. Nowotny *et al.*,¹ in working with the ternary system Mo-Si-C, proposed two possible phase diagrams for the system Si-C. These were for pressures less than one atmosphere and were based on a limited number of experimental points so that a decision between the two could not be made. The solubility of C in liquid Si has been measured by Hall² up to 1710°C. Others³ have found Si as an impurity in natural diamond, although the conditions of formation are of course unknown. We present here some solubility measurements in liquid Si up to 2900°C, and a proposed phase diagram for the system.

Experimental Procedure

The experiments were carried out in a 50-kw graphite resistance furnace heated by 20 v maximum, 60-cy

¹ Nowotny, Parthé, Kleffer, and Benesovsky, *Monatsh. Chem.* 85, 255 (1954).

² R. N. Hall, *J. Appl. Phys.* 29, 914 (1958).

³ F. G. Chelley, *Am. Mineralogist* 27, 20 (1942); F. A. Raai, *ibid.* 42, 354 (1957).

ac. This was enclosed in a water-cooled pressure vessel. Argon at a pressure of 35 atmos was used to reduce the tendency of the silicon to evaporate. The vapor pressure of silicon is about one atmosphere at 2800°C over both Si⁴ and SiC.⁵ Figure 1 shows the arrangement of the silicon container, heater, and shields which were used above 2000°C. The entire assembly was of graphite and was supported from the current terminals. On the basis of melting point measurements on iridium wires, the temperature variation over the container was believed to be not over $\pm 25^\circ\text{C}$ from the value at the point of measurement. The mounting of the container within the heater tube was such that no current passed through the Si charge. In this way, changes in the state of the Si, and hence in its electrical resistivity, did not affect the temperature distribution.

The Si was du Pont hyperpure grade, ground with a Pyrex mortar and pestle, screened, and leached with HF to remove any glass contamination in the Si from the mortar. The graphite container was filled with 100 mesh Si (about 0.5 g) and closed with a graphite end plug. No carbon was added; the carbon which was

⁴ R. E. Honig, *J. Chem. Phys.* 22, 1610 (1954).

⁵ Drowart, de Maria, and Inghram, *J. Chem. Phys.* 29, 1015 (1958).

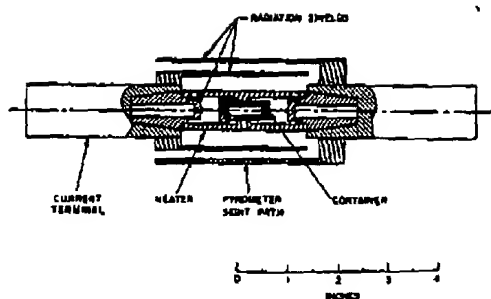


Fig. 1. Graphite resistance furnace (axial cross section).

taken into solution by the liquid silicon came from the walls of the container.

After assembly of the furnace, the pressure vessel was evacuated; it was then refilled twice with argon to a pressure of 20 atmos, vented to atmospheric pressure each time, and finally filled to the operating pressure. A manostat maintained the pressure within ± 1 atmos.

The length of time that the charge was kept at the operating temperature was a compromise. A long time ensured equilibrium, but for long times the Si loss became excessive with graphite containers. Usually temperature was kept constant at the desired value for periods of one-half to two minutes. No dependence of the C solubility upon the duration of run was observed. The charge was cooled as rapidly as possible after the run by simply shutting off the power to the furnace. Initial cooling rates of $50^\circ\text{C}/\text{sec}$ were typical.

Analysis

The carbon which was in solution in the liquid silicon at high temperatures crystallizes as SiC upon cooling. The Si slug containing the SiC was recovered by oxidizing away the graphite reaction vessel at 1100°C in an O_2 atmosphere. Less than 0.2 mg of SiO_2 was produced by this treatment. The original charge of Si could be accounted for in four portions:

1. Some had reacted with the container, forming a microcrystalline mass of SiC within the pores of the graphite container. Use of a dense graphite ($1.90 \text{ g}/\text{cm}^3$)* for the containers was necessary to avoid excessive losses in this way. This loss occurred mainly during the furnace warmup after the silicon liquified, and in unfavorable cases amounted to over 50 percent of the initial charge.

2. Some remained within the container as elemental Si, frozen into a small slug. This generally ranged from 10 percent to 60 percent of the initial charge of 500 mg, depending on the porosity of the container.

Some precipitated as SiC during cooling of the furnace. Most of the SiC was enclosed within the frozen

mass of Si, although some may have segregated to the surface of the Si. No free C remained within the piece of silicon, as determined both by microscopic examination and by chemical analysis of the residue which remained after the silicon was removed by etching.

4. Little if any Si was lost by evaporation because of the blanketing effect of the argon and the low porosity of the graphite container.

The slug of elemental Si containing the precipitated silicon carbide was lightly sandblasted to remove SiC which was formed in the walls of the graphite container and adhered to the surface of the slug. A thin layer of silicon (less than 25μ) was removed from the slug during the sandblasting. After the sandblasted slug was weighed, the Si was etched away in a mixture of 1 part HF to 3 parts HNO_3 . The SiC residue, which was not attacked by the etch, was dried and weighed. The carbon solubility at the operating temperature of the furnace was computed from the ratio of the mass of SiC to the mass of Si in the slug.

The major source of error in this procedure was the separation of the SiC formed by surface reaction with the container from that formed by reaction with dissolved carbon. It is felt that the experiments done in graphite gave a lower limit to the solubility of C in Si, because some dissolved SiC which was segregated to the surface during cooling may have been lost in sandblasting. Because only a thin layer was removed it is believed that at least 90 percent of the SiC is retained in the slug. Also, from the reproducibility of experiments one concludes that this loss was not serious.

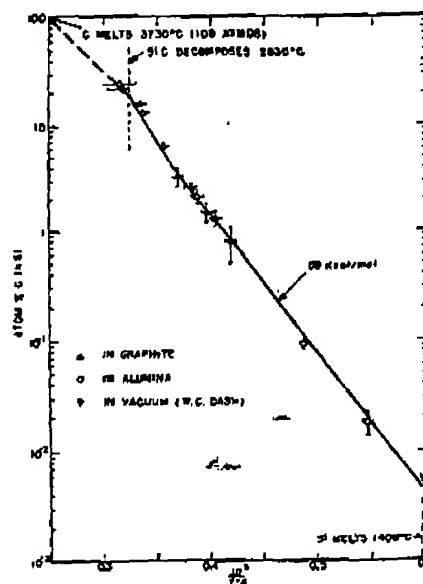


Fig. 2. The solubility of C in Si as a function of temperature.

* We are indebted to R. L. Shepard, of the National Carbon Company Research Laboratories, for some samples of a suitable high-purity graphite.

Two of the measurements were made at different heater and this change was not included in the total amount of SiC which was dissolved. These data were included in order to provide a check on the SiC content of the Si melt. A measurement of the SiC which was redeposited on the bottom of the furnace was made by W. C. Dash using a pedestal clamped at the bottom of the furnace. The SiC of about 4.1 mg was melted and sank until it reached the bottom of the furnace. After about 10 minutes the furnace was cooled and the SiC was etched and again the weight loss and the mass solubility to be found. silicon at the melting p

Temperature

All temperature measurements were made by Leeds & Northrup type which had been recently calibrated against a pure (L) scale. Corresponding scales have at most a 1 percent transmission through the furnace were made separately inside the furnace as a check in place and removed for correction to be made. The operation of the surface of the furnace at the bottom of a hole is deep. The rough walls of the furnace are not as good as a blackbody. The wall of the Si container was at the operating temperature by direct measurement which had a hole in the container which had a hole in the container.

* W. C. Dash, J. Appl. Phys.

SOLUBILITY OF CARBON IN SILICON AND GERMANIUM

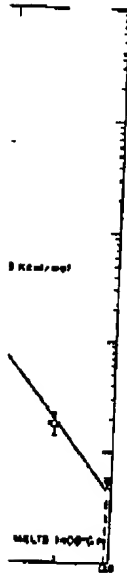
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s procedure was the urface reaction with reaction with dis- xperiments done in olubility of C in Si, as segregated to the been lost in sand- was removed it is the SiC is retained ucibility of experi- as not serious.



on of temperature

Two of the measurements at temperatures below 1000°C were made in the same furnace, but with a different heater and an Al_2O_3 container (see Fig. 2). This change was necessary because a larger melt (10–20 g) was needed to dissolve a measurable amount of carbon. In the latter experiments, a weighed crystal of SiC was included in the melt, and its weight loss was used to determine the solubility. As a check, the SiC content of the Si melt was also found. About 2/3 of the SiC which was dissolved from the crystal was recovered. The total amount of SiC lost from the crystal was 5–10 mg. These experiments in ceramic containers were done in order to provide a comparison with those carried out in graphite. These data are upper limits to the solubility, because all the SiC lost from the weighed piece was considered to have gone into solution even though some redeposition of SiC on the walls of the container may have occurred during the run. The agreement between the measurements performed in Al_2O_3 and those performed in graphite is good, as can be seen from Fig. 2. A measurement of the solubility at the Si melting point was made by W. C. Dash. This was performed in vacuum using a pedestal technique.⁹ A vertical bar of Si, clamped at the bottom, was heated at the top until a portion melted. Then a carefully weighed crystal of SiC of about 4.1 mg was inserted from above into the melt and sank until it rested at the liquid-solid interface. After about 10 min the melt was refrozen. The Si which surrounded the SiC crystal was removed by etching and again the SiC crystal was weighed. The weight loss and the mass of Si in the melt enabled the solubility to be found. The carbon solubility in liquid silicon at the melting point is $3.0 \pm 0.3 \times 10^{-3} \text{ A/cm}^3$.

Temperature Measurement

All temperature measurements were made with a Leeds & Northrup type 8622-C optical pyrometer which had been recently standardized. Calibration errors are known to within $\pm 2^\circ\text{C}$ on the low-temperature (L) scale. Correspondingly the higher temperature scales have at most a $\pm 10^\circ\text{C}$ error. Measurements of transmission through the sight tube window of the furnace were made separately using a tungsten strip lamp inside the furnace as a source, with the window alternately in place and removed. This allowed an accurate correction to be made for transmission losses. During operation the surface of the Si container was visible at the bottom of a hole in the heater tube two diameters deep. The rough walls of the hole and the high emissivity of graphite both tended to make the hole equivalent to a blackbody. The temperature drop across the wall of the Si container was found as a function of temperature by direct measurement on an empty container which had a hole through to the interior. This hole was so positioned that both internal and

⁹ W. C. Dash, J. Appl. Phys. 29, 736 (1958).

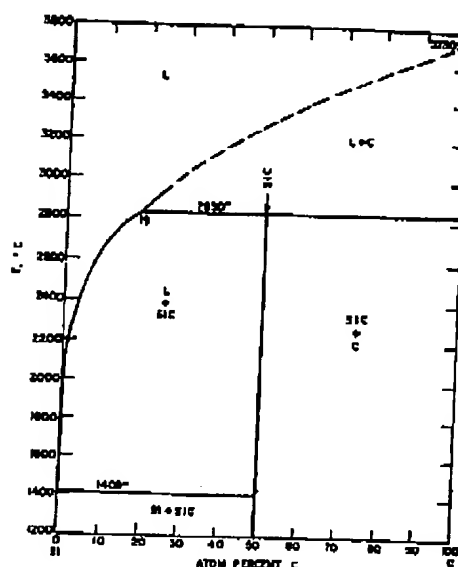


Fig. 3. Phase diagram of the system Si-C for pressures above 108 atmos.

surface temperatures could be measured at the same time. A useful check on the pyrometer was obtained from a plot of heater current vs absolute temperature squared. Above about 1700°C this plot was linear, indicating that radiation was by far the most important mechanism of energy loss.

As a final test, the melting points of Ir (2454°C) and Mo (2622°C) were measured, care being taken to avoid contact between the metal and carbon. We obtained 2446°C and 2634°C, respectively.

Pyrometry errors may be estimated as follows: setting and calibration errors on the instrument, $\pm 10^\circ\text{C}$; window transmission uncertainty, $\pm 20^\circ\text{C}$; and error in the temperature drop across the reaction container wall, $\pm 10^\circ\text{C}$.

Results

The solubility of C in Si as a function of temperature is given in Fig. 2. Some curvature may be noted at concentrations of five atom percent and more, presumably because the solution is nonideal. We find the solubility to be about 1/5 of that reported by Hall.³ Recent experiments by J. H. Racette⁷ of this laboratory, in a fused quartz apparatus similar to that used by Hall, indicate that this discrepancy was most likely due to the presence of sufficient oxygen in the melt in Hall's experiment to remove much of the dissolved carbon as CO or CO_2 . The oxygen presumably came from the quartz (SiO_2). In that case the carbon solubility would have appeared to be too high because the SiC crystal placed in the melt continuously lost carbon. Racette's

⁷ J. H. Racette (private communication).

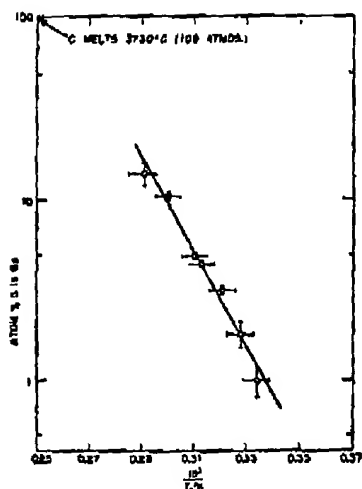


FIG. 4. The solubility of C in Ge as a function of temperature.

experiments show an apparent increase in solubility as the duration of the experiment is increased.

The linear portion of the curve below 1A% carbon as a slope corresponding to an enthalpy of solution of 9 kcal/mole, as calculated from the expression

$$x = \exp[(\Delta H/R)[(1/T) - (1/T_m)] \quad (1)$$

In this equation, x is the fractional atomic concentration of carbon in silicon at temperature T , ΔH is the enthalpy of solution, R is the gas constant per mole, and T_m is the temperature intercept at unit carbon fraction obtained by extrapolation of the linear portion of the solubility curve. Depending on how the line is drawn through the data points, ΔH may vary ± 3 kcal/mole.

In the course of these experiments it seemed worthwhile to explore as much of the phase diagram of the system Si-C as was accessible. Attempts were made to melt SiC in graphite containers similar to those used for the solubility experiments. The ambient pressure was well in excess of the decomposition pressure in all experiments. A transformation of some originally light green, type 6H, hexagonal, 120-mesh, SiC grain to a markedly different structure occurred at temperatures of $2830 \pm 40^\circ\text{C}$ and above. The SiC found after the transformation was cubic, as analyzed by x-rays. Heating to lower temperatures resulted only in a sintering together of the grains without any gross structural change. This experiment was repeated with cubic SiC grain as the initial charge. It decomposed at the same temperature, and the SiC found after the transformation was also cubic. From this, and from evidence gained from other experiments with SiC at elevated temperatures, we conclude that SiC decomposes without congruent melting, resulting in a silicon-rich liquid in

equilibrium with graphite at temperatures from 2830°C to at least 3160°C . The liquid composition at this latter temperature is approximately 50 atom percent carbon. When the liquid resulting from the decomposition of SiC is cooled below the decomposition temperature, the Si reacts with the dissolved and suspended carbon to form the cubic SiC found by x-ray analysis.

Experiments have also been performed in which cubic SiC grains have been heated in graphite tubes in this furnace to temperatures slightly below 2830°C . At the end of a run lasting several minutes the original cubic SiC is still present although slightly sintered together. Other experiments have been conducted in this apparatus in which both cubic and hexagonal crystals of SiC have been grown side by side from the vapor phase at temperatures of 2600°C . These growing experiments lasted several hours. It is therefore concluded that cubic SiC is stable at these temperatures and does not readily transform into hexagonal SiC in contrast to the conclusions of Baumann.¹ However, it should be noted that the conditions in the present experiments are not the same as those found in commercial SiC furnaces.

Difficulty was encountered in attempting to extend the solubility measurements above 3000°C . Even the high-density graphite containers would not hold liquid silicon at these temperatures. Furthermore the interpretation of the chemical analysis became difficult because the sample after cooling to room temperature usually contained silicon carbide, silicon, and carbon in a carbon container.

The phase diagram shown in Fig. 3 incorporates the

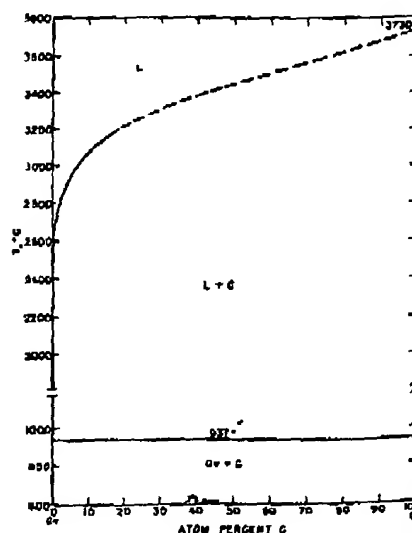


FIG. 5. Tentative phase diagram of the system Ge-C for pressures above 108 atmos.

¹ H. N. Baumann, J. Electrochem. Soc. 99, 109 (1952).

findings described given by Basset,² as by Pell.¹⁰ It confirms the proposed by Pell.¹¹ Note that it is assumed to be high and always present. pure carbon at 3730°C over carbon at the required pressure of 15 atmos a temperature reached.⁴

EXPERIMENT

The solubility of carbon in germanium has apparently not been previously shown in Fig. 3. Containers to temperature and have analyzed the limit of 3170°C was germanium evaporation maximum argon pressure below 2780°C the air limited volume of liquid measure accurately. refined; the container was isopic graphite with

The samples were in graphite containers. After weighing, the sample HF in three parts precipitated graphite

² J. Basset, J. phys. radiat.
¹⁰ E. M. Pell, J. Phys. Chem.
¹¹ M. Hansen, Constitution of alloys, p. 378.

SOLUBILITY OF CARBON IN SILICON AND GERMANIUM

1555

temperatures from 2830°C position at this latter atom percent carbon. the decomposition of position temperature, and substituted carbon ray analysis.

formed in which cubic graphite tubes in this below 2830°C. At the times the original cubic tubes sintered together. ducted in this apparatus. crystals of SiC in the vapor phase at growing experiments concluded that cubic ; and does not readily contrast to the con- should be noted that eriments are not the SiC furnaces.

attempting to extend e 3000°C. Even the could not hold liquid hermore the interpre- ame difficult because temperature usually id carbon in a carbon

Fig. 3 incorporates the



system Ge-C for pres-

79, 109 (1952).

findings described above, the melting point of carbon given by Basset,⁹ and the melting point of silicon given by Pell.¹⁰ It confirms the general features of the diagrams proposed by Nowotny *et al.*¹ and quoted by Hansen.¹¹ Note that in Fig. 3 the ambient pressure is assumed to be high enough that solid or liquid phases are always present. This will be at least 108 atmos for pure carbon at 3730°C, since this is the vapor pressure over carbon at the triple point.⁹ At lower temperatures the required pressure will be less. With a pressure of 15 atmos a temperature of about 3400°C can be reached.⁴

EXPERIMENTS WITH GERMANIUM

The solubility of carbon in germanium has apparently not been previously reported. Using the furnace shown in Fig. 1, we have heated Ge in graphite containers to temperatures between 2780°C and 3170°C and have analyzed the results. The upper temperature limit of 3170°C was set by the requirement that the germanium evaporation rate be kept low with a maximum argon pressure of 55 atmos. At temperatures below 2780°C the amount of carbon dissolved in the limited volume of liquid germanium was too small to measure accurately. The Ge had been previously zone refined; the containers were machined from spectroscopic graphite with a density of 1.7 g/cm³.

The samples were recovered by cracking apart the graphite containers. The germanium did not adhere to the graphite, and was in the form of a shiny slug. After weighing, the slug was etched in a mixture of one part HF in three parts HNO₃. The residue was partly precipitated graphite in the form of small flakes and

partly Ge. Apparently the etch was unable to leach all the Ge from the graphite flakes because of the hydrophobic nature of graphite. The residue was therefore roasted in Cl₂ at 1000°C in a quartz crucible to remove the Ge by the formation of volatile GeCl₄. After the remainder of the residue was weighed, it was then burned in O₂ at 1000°C to form CO₂. No evidence of GeO or GeO₂ was found after the oxidation, indicating that the residual Ge had indeed been removed from the graphite.

The results are shown in Fig. 4. If the solubility line were extrapolated to the melting point of Ge, the concentration of C in the liquid would be about 10²⁰ atoms per cm³. This is probably a lower limit. The carbon-germanium system is nonideal and such an extrapolation is inaccurate. (This extrapolated solubility is a factor of about 10²⁰ less than the carbon concentration in liquid silicon at its melting point. No evidence of compound formation between carbon and germanium was found up to temperatures of 3170°C. The C-Ge phase diagram therefore appears to be quite simple, and a tentative sketch is shown in Fig. 5. A simple eutectic point probably exists very slightly below the melting point of Ge at 937°C.¹² This is qualitatively similar to the C-Pb and C-Sn systems as deduced from the solubility studies of C in Pb and in Sn at temperatures up to 2300°C.¹³)

ACKNOWLEDGMENTS

We are much indebted to W. C. Dash for his measurement of the solubility of C in Si at the Si melting point. Also, we wish to thank R. N. Hall and J. H. Racette for many helpful discussions.

⁹ J. Basset, *J. phys. radium* 10, 217 (1939).

¹⁰ E. M. Pell, *J. Phys. Chem. Solids* 3, 77 (1957).

¹¹ M. Hansen, *Constitution of Binary Alloys* (1958), second edition, p. 378.

¹² E. S. Greiner and P. Breidt, *Trans. Am. Inst. Mining Met. Engrs.* 203, 187 (1955).

¹³ O. Ruff and B. Bergdahl, *Z. anorg. u. allgem. Chem.* 106, 76 (1919).

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THE Si-C AND Ge-C PHASE DIAGRAMS*

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Abstract—The solubility of carbon in silicon has been measured over the temperature range 1408°C to 2900°C. The enthalpy of solution is 59 ± 3 kcal/mol. A phase diagram for the system Si-C is presented, embodying these solubility data as well as the results of other high temperature experiments with silicon carbide. It is found that SiC possesses a peritectic point at $2830 \pm 40^\circ\text{C}$. These studies were carried out in argon at pressures as high as 35 atm. Solubilities of carbon in germanium were measured in the temperature range 2780°C to 3170°C, at argon pressures up to 55 atm.

In the literature on silicon carbide, one finds reference to the fact that SiC decomposes at high temperatures. The temperature at which this occurs has been variously cited, and values from 2200 °C^{4,5} to 2700 °C^{6,7} may be found. This wide range, and the fact that most, if not all of these studies were done under non-equilibrium conditions, leads to the belief that a true decomposition of bulk SiC is not what has been observed, but instead a dissociation of the surface caused by preferential evaporation of silicon from the SiC. The heat of formation data of Humphrey *et al.*², when extrapolated to higher temperatures, indicate that decomposition may occur near 2600 °C. If SiC could be melted without the occurrence of bulk decomposition, then crystals could be grown from the melt. Even if SiC does not possess a melting point, further knowledge of the phase diagram of the system Si-C would be useful in crystal growing work.

To investigate the behavior of SiC at elevated temperatures and pressures, the furnace shown in Fig. 1 was built. A water-cooled pressure vessel surrounds the graphite furnace assembly seen in the center. The vessel will hold a pressure of as much as 1000 lb/in.²; this dense atmosphere retards the evaporation of silicon which would otherwise be quite troublesome.

Figure 2 shows a cross-section of the furnace assembly. All the parts are made of graphite. The two current terminals support a tubular heater, two radiation shields, and a container which was used in the experiments on the solubility of carbon in silicon. The container is supported in such a way that it carries no current. About 50 kW is available to heat this assembly, enabling temperatures of about 3500 °C to be reached.

Optical pyrometry is the only reasonably accurate way of measuring temperature above 1900 °C, which is the limit for platinum-alloy thermocouples. A sight tube and window are provided in the side of the pressure vessel, and openings are left in the radiation shields and heater tube to allow measurement of the internal temperature of the furnace. Corrections to the pyrometer reading must be made for window transmission

* A more complete account of this work has been accepted for publication in the *Journal of Chemical Physics*.

The Si-C and Ge-C Phase Diagrams

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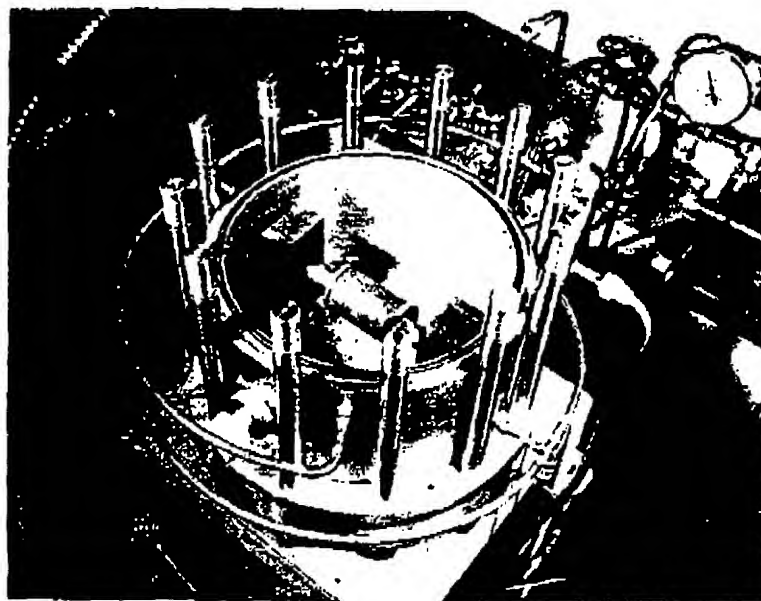


FIG. 1. Interior view of pressure vessel, showing high-temperature furnace in place.

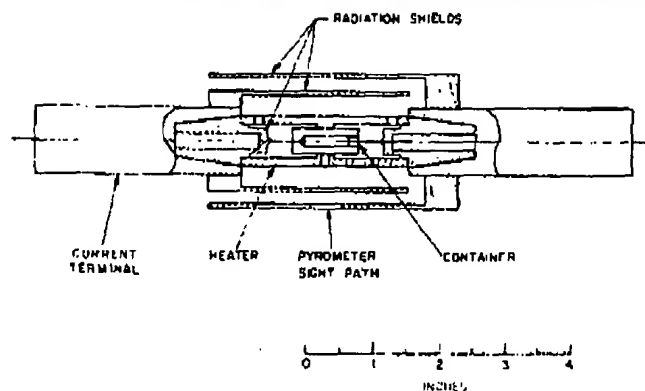


FIG. 2. Cross-section sketch of furnace assembly.

and the emissive properties of the surface whose temperature is to be found. As a check, the melting points of Ir and Mo were measured. The temperatures found were within

$\pm 10^\circ\text{C}$ of the published values. Under ordinary circumstances, temperature measurements are believed to be within $\pm 30^\circ\text{C}$ of the true value except at the very highest temperatures (say 3000 or more) where errors may amount to 50°C .

To determine the solubility of C in Si, the inner container was filled with Si. The container was sealed with a tight fitting plug, assembled into the furnace and heated to some temperature between 2100 °C to 2900 °C. Thermal equilibrium was achieved quite rapidly, and the sample was held at a fixed temperature for one or two minutes, after which the power was shut off. Then the furnace temperature decreased rapidly by radiation cooling and the Si inside froze. The graphite container was removed from the furnace and burned away from the Si by heating in O_2 . The original charge of Si can be accounted for as follows:

1. Some had reacted with the container, forming a micro-crystalline mass of SiC within the pores of the graphite.
2. Some remained within the container as elemental Si, frozen into a slug. This ranged from 10 to 60 per cent of the initial charge of 500 mg.
3. Some combined with the dissolved C in the liquid Si, and precipitated within the frozen slug of Si as SiC. No free C was found inside the slug of Si.
4. Very little, if any, Si was lost by evaporation because of the blanketing effect of the high pressure argon atmosphere, and the low permeability of the high density graphite.

The loosely adhering SiC, formed by reaction with the container, was carefully removed from the frozen slug. The slug was then weighed, etched in HF-HNO₃ to remove the Si, and the remaining SiC found inside the Si slug was weighed. With these data the solubility could be found for the temperature in question.

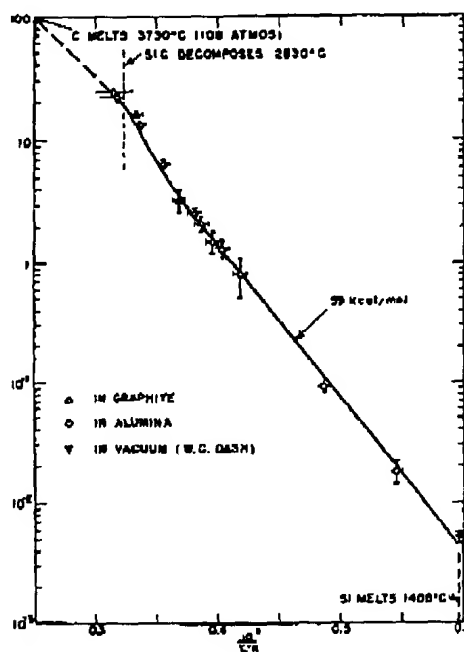


FIG. 3. The solubility of carbon in silicon as a function of reciprocal temperature.

The Si-C and Ge-C Phase Diagrams

27

Below 2000 °C the solubility is so low that an accurate determination with 500 mg of Si solvent was impossible. Two runs of 10 and 20 g melts were done in recrystallized alumina crucibles, with a different furnace arrangement in the pressure vessel. Here a weighed single crystal of SiC was included in the melt, and its weight loss combined with the known weight of Si in the melt enabled the solubility to be found.

Finally, Dash² performed a measurement of the solubility at the Si melting point, again by measuring the weight loss of a single crystal of SiC. His melt of Si was supported on top of a pedestal¹ of Si in vacuum. The SiC crystal rested on the liquid-solid interface, so there is little question of temperature measurement accuracy.

These data are all summarized in Fig. 3. The consistency of the results of the various experiments is good. Two points of particular interest are the solubilities of carbon in liquid Si at the Si melting point, 5×10^{-3} atom per cent (5×10^{17} C/cm³ Si), and at the decomposition temperature of 2830 °C. This is the maximum temperature at which SiC could be grown from a Si solution, and the carbon content of the melt here is 19 atom per cent. This high solubility indicates that growth from solution is feasible. The vapor pressure of Si over Si² and over SiC³ at this temperature is of the order of 1 atm and rising rapidly, so the need for a pressurized atmosphere to maintain stable conditions for any length of time is apparent.

Another way of plotting these data is on a temperature vs. composition phase diagram, Fig. 4. The behavior of SiC at the decomposition temperature is more clearly seen. This temperature, 2830 °C, was found by heating samples of SiC grain in containers such as

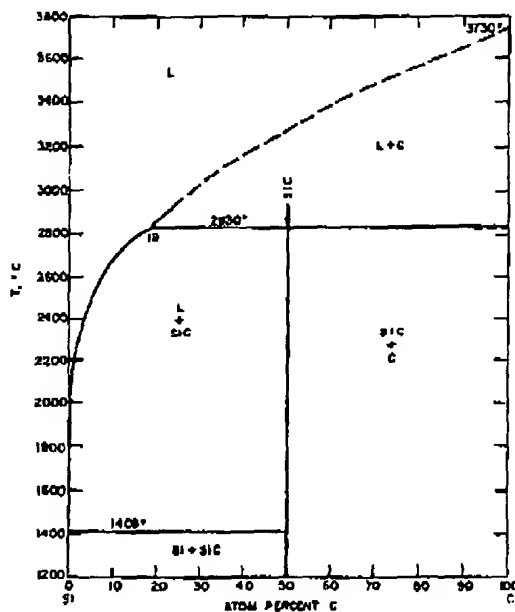


FIG. 4. Phase diagram of the binary system Si-C.

were used for the solubility measurements. All samples whose temperature exceeded this value were decomposed, while none were affected which were cooler. Two fortunate trials, one with hexagonal SiC and one with cubic, were half decomposed and half not, so the temperature was determined as closely as pyrometry errors will allow.

Some measurements have also been performed on the C solubility in Ge, in a manner similar to that used for Si. Figure 5 shows a tentative Ge-C phase diagram based on these measurements. Solubilities of 12 per cent at 3170 °C were reached, where the Ge vapor pressure is several atmospheres. No evidence of compound formation was seen. A very rough extrapolation of these data to the melting point of Ge can be made, indicating that the C solubility in liquid Ge at this temperature is of the order of 10^{10} C/cm³ Ge.

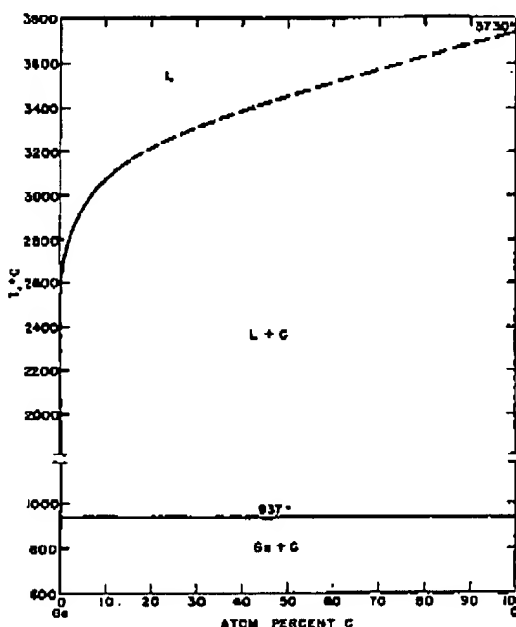


FIG. 5. Tentative phase diagram of the binary system Ge-C.

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